

PATENT SPECIFICATION

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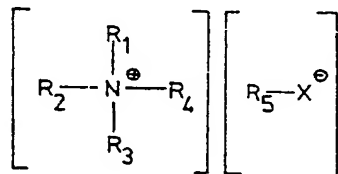
(54) OIL SOLUBLE FUNGICIDAL QUATERNARY AMMONIUM SALTS

(71) We, NIPPON OIL COMPANY LIMITED, a Japanese body corporate of 3—12, 1-chome, Nishi-Shimbashi, Minato-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 This invention relates to novel oil soluble compounds suitable for use as fungicides.

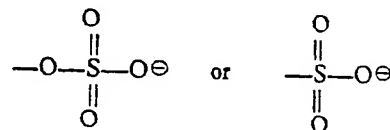
It is a well known fact that some quaternary ammonium salts such as alkyl quaternary ammonium chlorides have a strong sterilizing power in an aqueous solution. As a result, these quaternary ammonium salts are widely used as fungicides. However, the quaternary ammonium salts, though soluble in water, are not suitable as fungicides to be used for oleophilic materials such as fats, hydrocarbon oils and high molecular weight compounds because they are hardly soluble in such oleophilic materials.

It has previously been discovered that ammonium salt type fungicides, which are cation surface active agents, considerably lose their sterilizing power in the presence of an anion surface active agent. The present invention is based on the discovery that certain quaternary ammonium salt type cation fungicides can retain their sterilizing power and also gain oil solubility by selecting a suitable anionic surface active agent and then reacting it with the quaternary ammonium salt type cation surface active agent.

The present invention provides an oil soluble compound of the general formula



wherein R_1 represents an aromatic hydrocarbon group having up to 22 carbon atoms. R_2 and R_3 , which may be the same or different, each represents an aliphatic hydrocarbon group having up to 8 carbon atoms, R_4 represents an aliphatic hydrocarbon group having 8 to 22 carbon atoms, R_5 represents an aliphatic hydrocarbon group having 6 to 20 carbon atoms or an aromatic hydrocarbon group having 7 to 20 carbon atoms and X^- represents



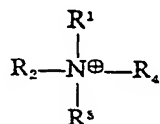
The preferred compounds are those in which R_1 represents an aralkyl group whose alkyl portion contains 1 to 12 carbon atoms and R_5 represents an alkaryl group having 7 to 18 carbon atoms. Particularly preferred are those compounds in which R_1 represents a benzyl group and R_2 and R_3 each represents a methyl group.

The oil soluble compounds of this invention can be used for various purposes. Because of their oil solubility, they are suitable as fungicides for protecting oil products such as jet fuel, kerosene, gas oil, fuel oil and lubricating oil from the harmful effects of bacteria. They are also effective as fungicides for protecting natural and synthetic high molecular weight compounds such as fibers, paints, plastics and rubber from the harmful effects of bacteria. Furthermore, the compounds do not exhibit a corrosive action on metals such as copper, steel and aluminium.

The fungicide of this invention is preferably used in a concentration of 10 to 10,000 ppm. In general, however, a concentration of about 50 ppm gives a satisfactory sterilizing effect, and at such concentrations there

are no adverse effects on the properties of the material to be sterilized.

The compounds of the invention may be prepared by a process which comprises reacting, in aqueous solution, a quaternary ammonium salt containing a cation of the formula:



wherein R_1 , R_2 , R_3 and R_4 are as defined above with a sulfonate or sulfuric acid ester salt containing an anion of the formula $[R_5-X^{\ominus}]$ wherein R_5 and X are as defined above.

The reaction is preferably carried out at normal temperatures and under normal pressures, the reaction temperature is preferably within the range of -10 to 300°C . The reaction rate is decreased if the temperature is lower than -10°C while a temperature exceeding 300°C is also undesirable because of causing side-reactions such as decomposition.

The quaternary ammonium salt may, for example, be a halide, sulfate, phosphate or nitrate, such as alkyl (mixed alkyl having 8—18 carbon atoms)-dimethylbenzylammonium, cetyl - methyl - ethyl - benzylammonium or cetyl - dimethyl - dodecyl - benzylammonium chloride, bromide, sulfate, nitrate or acetate.

Sulfonates suitable for use in the process are, for example, salts (such as alkali metal or alkaline earth metal salts) of alkylsulfonic acids, alkenylsulfonic acids, straight- or branched-chain alkylbenzenesulfonic acids, naphthalenesulfonic acids, alkylnaphthalenesulfonic acids or diarylalkanesulfonic acids.

Examples of suitable sulfuric acid esters are salts (such as alkali metal or alkaline earth metal salts) of monoesters such as sulfuric acid esters of straight- or branched-chain primary higher alcohols or sulfuric acid esters of secondary higher alcohols of straight- or branched-chain olefins. The concentrations of the quaternary ammonium salt and the sulfonate or sulfuric acid ester salt in the solutions are preferably 0.1 to 50%, especially 1 to 10% by weight, based on the weight of water. If desired, more than one anionic material can be used. Specific examples of sulfonates or sulfuric acid esters which may be used are straight- or branched-chain sodium dodecylbenzenesulfonate, sodium nonylnaphthalenesulfonate, sodium decanesulfonate, potassium dodecylbenzenesulfonate, lauryl alcohol sulfuric acid monoester sodium salt, stearyl alcohol sulfuric acid monoester sodium salt, 1-methyldecyl alcohol

sulfuric acid monoester sodium salt and n-hexyl alcohol sulfuric acid monoester sodium salt. 60

The reaction product is hardly soluble in water, and is therefore dispersed as a precipitate or colloid in an aqueous solution. The product can be separated directly after allowing the reaction mixture to stand, or it can be extracted by adding an organic solvent insoluble in water such as benzene or hexane to the reaction system. The extracted reaction product can be isolated in the form of a paste, wax, oil or solid by removing the organic solvent. 65 70

The sterilising power of reaction products was demonstrated by dissolving the reaction product in mineral oil wherein bacteria could grow. After adding an inorganic culture medium containing N, P, K, Fe and Mg to the resulting solution, bacteria which consume mineral oil were incubated in the medium, and the state of growth of the bacteria was examined. This test is described in the following Examples which illustrate the invention. 75 80

EXAMPLE 1.

350 grams of a 10% aqueous solution of straight-chain sodium dodecylbenzenesulfonate were added to 354 grams of a 10% aqueous solution of alkyldimethylbenzylammonium chloride (the alkyl group was a mixture having 8—18 carbon atoms), followed by shaking for 1 minute at room temperature. After further adding 350 ml. of benzene, shaking for 2 minutes and leaving the mixture to stand the benzene layer was separated to remove the benzene by evaporating under a reduced pressure. The white reaction product was obtained in a yield of 95% based on the theoretical value. The product having a melting point of $83-84^{\circ}\text{C}$ was identified as the dodecylbenzenesulfonic acid complex of alkyldimethylbenzylammonium by infrared spectroscopic and NMR analyses. 85 90 95 100

EXAMPLE 2.

350 grams of a 10% aqueous solution of a branched-chain type sodium dodecylbenzenesulfonate were added to 382 grams of a 10% aqueous solution of alkyldimethylbenzylammonium chloride (the alkyl group was a mixture having 8—22 carbon atoms), followed by shaking for 1 minute at about 20°C . After further adding 350 ml of hexane, shaking for 2 minutes and leaving the mixture to stand, the hexane layer was separated to remove the hexane by evaporating under a reduced pressure. The white reaction product having a melting point of $86-87^{\circ}\text{C}$ was obtained in a yield of 94% based on the theoretical value. The product was identified as the dodecylbenzenesulfonic acid complex of alkyldimethylbenzylammonium by the same analyses as those in Example 1. 105 110 115 120

EXAMPLE 3.

356 grams of a 5% aqueous solution of sodium nonyl-naphthalenesulfonate were added to 340 grams of a 5% aqueous solution of nonylethylpropylbenzylammonium chloride, followed by shaking for 1 minute at about 30° C. After further adding 350 ml of benzene, shaking for 2 minutes and leaving the mixture to stand, the benzene layer was separated to remove the benzene by evaporating under a reduced pressure. The white reaction product was obtained in a yield of 96% based on the theoretical value. The product was identified as the nonyl-naphthalene-sulfonic acid complex of nonylethylpropylbenzylammonium by the same analyses as those in Example 1.

EXAMPLE 4.

In the same manner as in Example 1, a reaction was conducted at room temperature using alkyldimethylbenzylammonium chloride (the alkyl group was a mixture having 8—18 carbon atoms) and lauryl alcohol sulfuric acid monoester sodium salt as the starting materials to obtain a white solid (having a melting point of 84—87° C) of the lauryl alcohol sulfuric acid monoester complex of alkyldimethylbenzylammonium in a yield of 97% based on the theoretical value.

EXAMPLE 5.

274 grams of a 20% aqueous solution of 1-methyldecylalcohol sulfuric acid monoester sodium salt were added to 354 grams of a 20% aqueous solution of alkyldimethylbenzylammonium chloride (the alkyl group was a mixture having 8—18 carbon atoms), followed by shaking for 1 minute at room temperature. 300 ml. of benzene were added, and the mixture was shaken for a further 2 minutes. After the mixture had been left to stand, the benzene layer was separated and the benzene was re-

moved from the separated benzene layer by evaporating under a reduced pressure. The yellow 1-methyldecylalcohol sulfuric acid ester complex of alkyldimethylbenzylammonium was obtained in a yield of 95% based on the theoretical value.

EXAMPLE 6.

By using dioctylmethylbenzylammonium chloride and n-hexylalcohol sulfuric acid monoester sodium salt as starting materials, the n-hexylalcohol sulfuric acid ester complex of dioctylmethylbenzylammonium was obtained in the same manner as in Example 2.

EXAMPLES 7 TO 12 AND COMPARATIVE EXAMPLE 1.

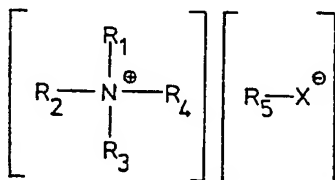
The test for examining the sterilizing power of the oil soluble fungicides synthesized in Examples 1 to 6 was conducted as follows:

The oil soluble fungicide was dissolved in kerosene, jet fuel, gas oil or fuel oil as indicated in the Table and 2 ml of this solution were added to a test tube having an inside diameter of 18 mm. After adding 2 ml of an inorganic culture medium containing 3 grams of NaNO₃, 1.0 gram of K₂HPO₄, 0.5 grams of KCl, 0.5 grams of MgSO₄·7H₂O and 0.01 gram of FeSO₄ per litre of distilled water, bacteria belonging to *Cladosporium* sp., *Penicillium* sp., *Aspergillus* sp., *Fusarium* sp., *Paecilomyces* sp., *Candida* sp. and *Pseudomonas* sp., were incubated at 30° C and cultivated by allowing the mixture to stand. After 90 days the mixture was inspected to see whether the bacteria were still living or not. For comparison, a test for examining the growth of bacteria was conducted by using kerosene, jet fuel, gas oil, fuel oil and lubricating oil including no fungicide. The results of these Examples are shown in the following Table.

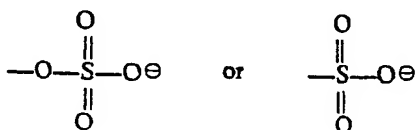
| Example | Type and concentration of fungicide added to mineral oil | Type of mineral oil used | Sterilizing effect (by cultivation at 30°C. for 90 days) | | | | | | |
|-----------------------|--|---|---|------------------------------------|--------------------|-----------------|---------------------|----------------|--------------------|
| | | | Cladosporium sp. | Penicillium sp. | Aspergillus sp. | Fusarium sp. | Paecilomyces sp. | Candida sp. | Pseudomonas sp. |
| 7 | Product of Experiment 1 50 ppm. | kerosene | - | No growth of bacteria was observed | | | | | |
| 8 | Product of Experiment 2 100 ppm. | jet fuel | - | - | Same as above | | | | - |
| 9 | Product of Experiment 3 30 ppm. | gas oil | - | - | Same as above | | | | - |
| 10 | Product of Experiment 4 150 ppm. | kerosene | - | - | Same as above | | | | - |
| 11 | Product of Experiment 5 100 ppm. | fuel oil | - | - | Same as above | | | | - |
| 12 | Product of Experiment 6 150 ppm. | kerosene | - | - | Same as above | | | | - |
| Comparative Example 1 | No fungicide was added. | kerosene, jet fuel, gas oil, fuel oil, and lubricating oil. | Large quantities of bacteria grew in all boundary surfaces between mineral oils and inorganic culture media | | | | | | |

WHAT WE CLAIM IS:—

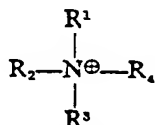
1. An oil soluble compound of the general formula



- 5 wherein R_1 represents an aromatic hydrocarbon group having up to 22 carbon atoms, R_2 and R_3 which may be the same or different, each represents an aliphatic hydrocarbon group having up to 8 carbon atoms, R_4 represents an aliphatic hydrocarbon group having 8 to 22 carbon atoms, R_5 represents an aliphatic hydrocarbon group having 6 to 20 carbon atoms or an aromatic hydrocarbon group having 7 to 20 carbon atoms and X^- represents



2. A compound according to claim 1 wherein R_1 represents an alkyl group whose alkyl portion contains 1 to 12 carbon atoms and R_5 represents an alkaryl group having 7 to 18 carbon atoms.
3. A compound according to claim 1 or 2 wherein R_1 represents a benzyl group.
4. A compound according to any one of the preceding claims wherein R_2 and R_3 each represents a methyl group.
5. A compound according to claim 1 specifically identified herein.
6. A process for producing a compound as claimed in any one of the preceding claims which comprises reacting, in aqueous solution, a quaternary ammonium salt containing a cation of the formula:



wherein R_1 , R_2 , R_3 and R_4 are as defined in claim 1 with a sulfonate or sulfuric acid ester salt containing an anion of the formula $[R_5 - X^-]$ wherein R_5 and X are as defined in claim 1.

7. A process according to claim 6 wherein the reaction is carried out at a temperature of from -10°C to 300°C .

8. A process according to claim 6 or 7 wherein the quaternary ammonium salt is a quaternary ammonium halide, sulfate, nitrate or acetate and the sulfonate or sulfuric acid ester salt is an alkali metal or alkaline earth metal salt of a sulfonic acid or a sulfuric acid monoester.

9. A process according to claim 6, 7 or 8 wherein the concentrations of the quaternary ammonium salt and of the sulfonate or sulfuric acid ester salt in the solutions are each 0.1 to 50% by weight, based on the weight of the water.

10. A process according to claim 9 wherein the concentrations are each 1 to 10% by weight, based on the weight of the water.

11. A process according to any one of claims 6 to 10 wherein the reaction is carried out at ambient temperature and pressure.

12. A process according to any one of claims 6 to 11 wherein the quaternary ammonium salt and/or sulfonate or sulfuric acid ester salt is any specifically identified herein as such.

13. A process according to claim 6 substantially as hereinbefore described.

14. A process according to claim 6 substantially as described in any one of Examples 1 to 6.

15. A compound according to claim 1 when prepared by a process as claimed in any one of claims 6 to 14.

16. A composition comprising, as oleophilic material, a fat, hydrocarbon oil or a natural or synthetic high molecular weight compound and, as fungicide, a compound as claimed in any one of claims 1 to 5 and 15 in a concentration of 10 to 10,000 parts per million.

17. A composition according to claim 16 substantially as hereinbefore described.

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